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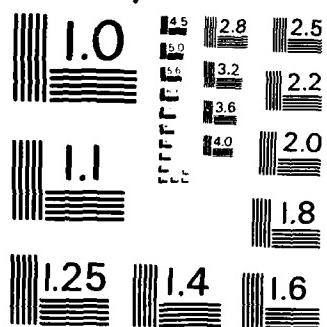
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vacuum deposited, which was subsequently exposed to a strong Lewis acid such as  $\text{AsF}_5$  in a controlled atmosphere. Two new polymers were produced using this method; these are polyfuran and polyazulene. Coherent thin films of poly bis(p-toluene sulfonate) diacetylene were successfully formed by modified Langmuir-Blodgett techniques using two methods: i) photopolymerization of the monomer film at the gas/liquid interface and then transfer to a solid substrate; and ii) transfer of the monomer film to the solid substrate and subsequent photopolymerization on the substrate itself. The films are multimolecular and about 100 Angstroms thick. The area of polymerization of the electrode/solution interface in an electrochemical cell is highly active because the prospect to produce high quality electroactive polymers of controlled ultrasubmicron thickness. Polyazulene was formed by anodic polymerization of azulene. Chemical doping of polymers is a highly active field of research, because the chemical doping has been successfully used to increase the electrical conductivities of several polymers as well as to induce conformational changes in some polymers. The nature of the iodine-nylon 6 complex was by resonance Raman spectroscopy. This work revealed the presence of both  $I_3^-$  minus and  $I_5^-$  minus species. The non-linear electroacoustic effect in organic materials was investigated by the novel technique of phonon echo. The phonon echo was investigated for the d-tartaric acid and its diammonium salt as well as for the Rochelle salt by using the two-pulse technique.

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FINAL PROGRESS REPORT

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The current year of support by AFOSR has produced significant research. The research was accomplished in the following areas: (i) Preparation of novel polymeric films using the specificity of interfacial phenomena, (ii) laser Raman investigation of the ultrastructure of doped polymers, and (iii) study of non-linear effects in organic materials.

Three interfacial methods have been used to produce thin polymeric films. These are (a) reactions at solid-gas interface, (b) Langmuir-Blodgett, and (c) electrochemical polymerization. The reaction at solid-gas interface involved the use of a thin monomeric film, vacuum deposited, which was subsequently exposed to a strong Lewis acid such as  $\text{AsF}_5$  in a controlled atmosphere. We produced two new polymers using this method; these are polyfuril and polyazulene. When yellow-brown furil, a compound rich in conjugated  $\pi$ -electrons, was exposed to  $\text{AsF}_5$  for 24 hours, it turned dark blue with a metallic lustre. Elemental analysis showed results consistent with a 6-7 unit polymer formation by hydrogen abstraction. The polymer was found to be stable up to 500°C. Prolonged heating at this temperature appears to produce a more rigid new structure. IR spectra of the reactant and the product are shown in Figure 1 which show differences, again, consistent with polymerization. X-ray powder diffraction studies conducted on both the polymer and the monomer reveal that the polymer produced is also crystalline and forms a lattice similar to that of the monomer. A manuscript reporting this work has been accepted for publication in the Journal of Polymer Science - Polymer Physics Edition. A copy of the preprint is enclosed. We have also used this method to produce polyazulene by reaction of azulene with  $\text{AsF}_5$ .

Coherent thin films of poly bis(p-toluene sulfonate) diacetylene were successfully formed by modified Langmuir-Blodgett techniques using two

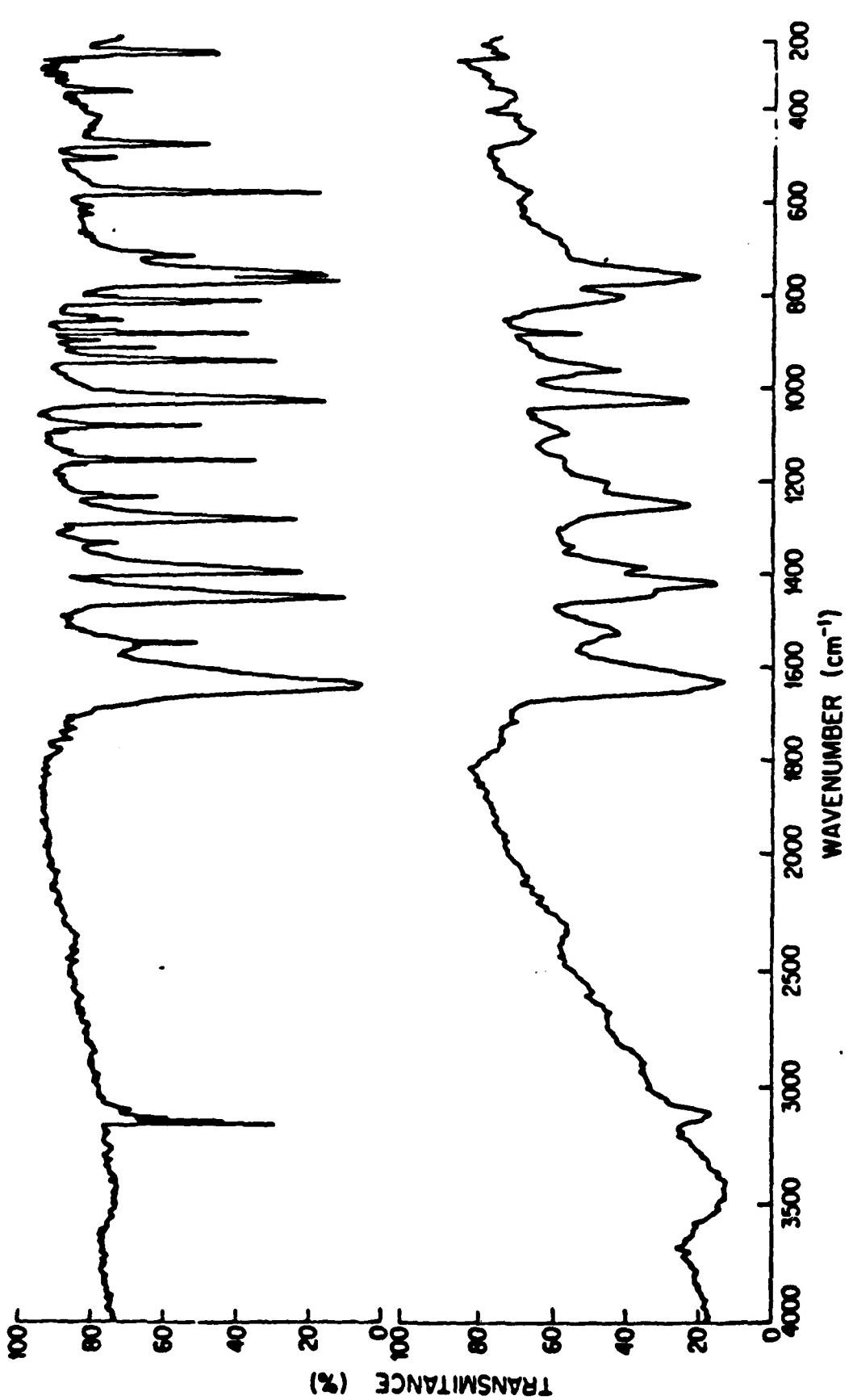


Figure 1

methods: (i) photopolymerization of the monomer film at the gas/liquid interface and then transfer to a solid substrate; and (ii) transfer of the monomer film to the solid substrate and subsequent photopolymerization on the substrate itself. The films thus obtained were characterized by traditional force-area Isotherms while on pure water subphases. Segments were transferred at either 1 dyne/cm or 10 dyne/cm surface pressure, in different stages of photopolymerization, to glass or germanium substrates. The films on the substrates were characterized by the methods of multiple attenuated internal reflection infrared spectroscopy, ellipsometry, contact potential measurement, and Laser Raman spectroscopy. Our results show that the films are multimolecular and about 100 Å thick. Of special interest was the observation of significant anisotropy of oriented dipoles, and the ability to obtain excellent spectral data for these very thin oriented films. Raman spectroscopic features are similar to those observed for the bulk polymer, even in the low frequency region. Polarized Raman spectroscopy confirmed the presence of local anisotropy in these films. A manuscript on this work has been accepted for publication in the Journal of Polymer Science - Polymer Physics Edition. A preprint is enclosed.

The area of polymerization of the electrode/solution interface in an electrochemical cell is highly active because of the prospect to produce high quality electroactive polymers of controlled ultrasubmicron thickness. We have studied polyazulene formed by anodic polymerization of azulene. This study was conducted in collaboration with Professor S. Bruckenstein of our department who is also supported by AFOSR. We have conducted IR spectroscopic studies of the oxidized and reduced forms of polyazulene. Polyazulene, in the oxidized form, is a radical cation with a counter anion such as  $\text{ClO}_4^-$  or  $\text{BF}_4^-$  incorporated. It behaves like a semiconductor. We

have found structural difference between the oxidized and the reduced forms. Also, the counter anion appears to affect the structure of polyazulene. It appears that the oxidized form of polyazulene has a porous structure which allows the exchange of anion. A manuscript reporting this work is under preparation.

Chemical doping of polymers is a highly active field of research, because the chemical doping has been successfully used to increase the electrical conductivities of several polymers as well as to induce conformational changes in some polymers. It has been suggested that when an amorphous film of an oriented  $\alpha$ -rich film of nylon-6 is treated with iodine, the development of an oriented Y-form takes place. We investigated the nature of the iodine-nylon 6 complex by resonance Raman spectroscopy. This work revealed the presence of both  $I_3^-$  and  $I_5^-$  species, the latter most likely in the form of an  $I_2/I_3^-$  complex. Polarization characteristics of the Raman Spectra showed that these two types of species are oriented differently. The  $I_2/I_3^-$  ions were suggested to be perpendicular to it. The  $I_2/I_3^-$  units were found to be in a more stable moiety than the  $I_3^-$  species. A correlation of the Raman results with those of X-ray diffraction was found to be satisfactory. A paper on this work has been accepted for publication in the Journal of Polymer Science-Polymer Physics Edition. A preprint is enclosed.

The non-linear electroacoustic effect in organic materials was investigated by the novel technique of phonon echo. The phonon echo, also called polarization or electroacoustic echo, was investigated for the d-tartaric acid and its diammonium salt as well as for the Rochelle salt by using the two-pulse technique. The dependence of the echo amplitude on the delay time was described both by the Anharmonic Oscillator model and the

model of coupled micromotions of the grains recently proposed by Pouget and Maugin. The echo under the experimental conditions behaves according to the small signal limit. The dependence of the damping factor on the pressure of the surrounding gas and the temperature was, respectively, used to measure an average speed of sound and to derive the mechanism of damping. In vacuum, the damping factor was found to depend on the square of the rf frequency as is expected from an intrinsic loss mechanism. A plot of the temperature dependence of the damping factor for d-tartaric acid exhibits a maximum. This maximum was explained by a thermally activated acoustic relaxation within the powder particles. The observed deuteration effect both on the shape and the position of the maximum points out the importance of hydrogen motions for the acoustic relaxation in these hydrogen-bonded solids. A reprint is enclosed.

Other areas of accomplished research are: (a) use of thin organic films in photovoltaic devices; (b) controlled polymerization of 2,5-distyrylpyrazine; and (c) laser Raman investigation of the drug-polymer conjugates of sulfathiazole and polyvinyl pyrrolidone.

The use of thin organic monomeric and polymeric films in various photovoltaic devices is a highly promising area of research. Our long range objective is to design and fabricate novel photovoltaic devices using submicron thin polymeric films. A fundamental understanding of the physics of the processes of energy transfer and charge-carrier generation is the first logical step towards such a goal. With this immediate objective in mind, we fabricated and studied a solar cell coated with thin films of pyrene. The current-voltage characteristics and the spectral response of thin film coated cells were studied. An increase in the solar cell efficiency was observed due to a combination of two effects: (1)

antireflective properties of the pyrene film, and (ii) a direct radioactive energy transfer from pyrene to silicon. This work has been published in the Journal "Solar Cells". A reprint is enclosed.

In order to formulate conditions under which defect free rigid polymers of a specific chain length can be produced, *in situ*, by polymerization in the solid state, it is necessary to understand the molecular mechanics of the polymerization process. With this objective, the molecular mechanics of photopolymerization of 2,5-distyrylpyrazine was investigated by a combination of Raman and electronic spectroscopic techniques. A stepwise photoreaction was used to stabilize an intermediate oligomer structure. This work has been published in the Journal of Polymer Sciences - Polymer Physics Edition. A reprint is enclosed.

Raman phonon spectroscopy was successfully used to study the various co-precipitates of sulfathiazole and the polymer polyvinyl pyrrolidone (molecular weight ~ 10,000). It has been reported previously that the drug-polymer co-precipitates show higher dissolution rates. In our Raman phonon study of the co-precipitates of various drug to polymer ratios we observe two different polymorphic forms of the drug. Our study does not reveal any complexation between the polymer and the drug. A reprint is enclosed. This work has also drawn the attention of the Food and Drug Administration. The principal investigator gave an invited talk on this work at the Food and Drug Administration.

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